

Reactive blending of polyamide with polyethylene: pull-out of in situ-formed graft copolymers and its application for high-temperature materials

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Abstract

Reactive blending of polyamide 6 (PA) with polyethylene (PE) having reactive sites, maleic anhydride (MAH content = 0.1 wt%), and glycidyl methacrylate (GMA content = 3–12 wt%), was carried out at 70/30 and 65/35 (PA/PE) blend ratios. Blend morphology evolved by reactive blending was analyzed by light scattering and transmission electron microscopy. The blends were then irradiated by electron beam. The degree of crosslinking was estimated by measuring the dynamic storage modulus at a temperature above melting point of PA. It was found that surface-to-surface interparticle distance τ was significantly reduced by the micelle formation via pull-out of in situ-formed graft copolymers. The blend with shorter τ was crosslinked by electron-beam irradiation at the lower dose level. A blend having the minimum τ ($\sim 0.2 \mu\text{m}$) was nicely crosslinked at a low dose level same as for PE, and even for the PA matrix system. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Reactive blending; Pull-out; Crosslinking

1. Introduction

Reactive compatibilization is an attractive strategy to improve properties of immiscible polymer blends. It has been implemented in blending of polyamide (PA) with polyolefin grafted with small amount of maleic anhydride (MAH) to produce the ‘super-tough nylon’ [1]. The compatibilization involves the interfacial modification process, which would result in lower interfacial tension, suppressed particle coalescence and enhanced adhesion [2]. The process is realized by generation of block or graft copolymers via in situ-coupling reaction at the interface between two phases during reactive blending. The interfacial effects are expected only when the copolymers stay at the interfacial region. The theory [3] predicts the stability of a rather symmetric block copolymer at the interface. The theory may work well at the quiescent state; however, it is getting obvious that it does not for the reactive blending (under dynamic condition). Nakayama et al. [4] experimentally showed that in a reactive blend of polystyrene- ω -COOH with poly (methyl methacrylate)- ω -epoxy, the block

copolymer formed at the interface during reactive blending left the interface and dispersed in bulk as micelles. Charoensirisomboon et al. [5] recently showed that the in situ-formed block copolymers don’t escape from the interfacial region by themselves but are easily pulled out by external shear forces. Then, the ‘pull-out or not’ of in situ-formed copolymers was found to be highly dependent on the copolymer architecture and the strength of shear forces in reactive PA/polysulfone and PA/polyethylene (PE) blends [6,7]. The block copolymers with linear chain structure (Fig. 1a) are more easily pulled out than the graft copolymers with inverse Y-shape (Fig. 1b). When the inverse Y-shape graft copolymer with long PA chain located in matrix was subjected to high shear force, it could also be pulled out. By contrast, the Y-shape graft copolymer (Fig. 1c) can be pulled out easily, except in the case of extremely long PA chain anchoring in the dispersed phase. Note that the graft copolymers of Y-shape and inverse Y-shape in Fig. 1 are supposed to have single graft site on one trunk chain, corresponding to the case of low content of functional group on the trunk chain (PE, PSU). Then, one can expect that the graft copolymer with multiple grafts and a trunk chain anchoring in the dispersed phase (Fig. 1d) would be more easily pulled out than that

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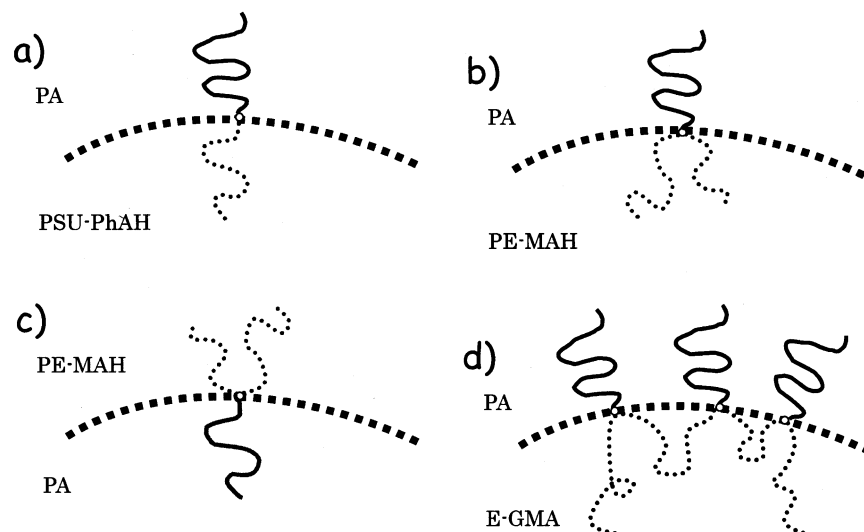


Fig. 1. Molecular architecture of in situ-formed copolymers at interface: (a) linear shape (block copolymer); (b) inverse Y-shape; (c) Y-shape; (d) multi-graft inverse Y-shape.

with inverse Y-shape during melt mixing. Following this expectation, the work in this paper was undertaken. In this work, we also tried to develop a high temperature material by applying the pull-out phenomenon and electron-beam crosslinking.

PA is a good engineering thermoplastic. However, the thermoplastics in general do not withstand at high temperatures above their melting points as structural materials do. For instance, in the case of fire, the plastic frame of glass window would melt down and the air will be led into the room resulting in greater fire. Also in the case of micro-electronics, when the lead-free solder is applied, the printed circuit board of PA, for example, would be subjected to serious distortion and/or melt-down. If the molded material is crosslinked by electron-beam irradiation, the high-temperature property could be considerably upgraded. However, PA is a hardly crosslinkable polymer, compared with PE (PE can be easily crosslinked by electron-beam and the crosslinked material is commercially used for electric cables). The problem would be solved by utilizing the pull-out or the micelle formation. The scenario is as follows.

As shown in Fig. 2a, when the in situ-formed graft copolymers are pulled out and a micelle locates between big particles, the surface-to-surface interparticle distance τ can be dramatically reduced (to τ' and τ''). The more micelles between two neighboring particles yield shorter τ so that the PA brush chains would start touching each other. When electron-beam is applied for such two-phase system and a very few tie points (dots in Fig. 2b) are generated in PA matrix, a three-dimensional network could be easily formed throughout the whole system via the well-crosslinked PE domains. Then, the system could be crosslinked by a low irradiation dose, compared with neat PA.

The τ can also be reduced by fattening the PE particles in PE-rich system, e.g. 40/60 PA/PE. In the PE-rich system, the in situ-formed graft copolymer chains are pulled out and the micelles are dispersed in PE matrix at early stage of reactive blending and then phase inversion takes place to render PE particles/PA matrix morphology [7,8]. The final PE particles occlude a lot of PA micelles (fatted) so that the τ can be reduced.

In this study, we carried out reactive blending of PA with PE with reactive sites, MAH and glycidyl methacrylate (GMA), using a miniature mixer. Morphology after reactive blending was studied by light scattering and transmission electron microscopy (TEM). The blends were then subjected to electron-beam irradiation. The degree of crosslinking was characterized in terms of the storage modulus above the melting point of PA measured by dynamic mechanical analysis.

2. Experimental

2.1. Materials

Two polyamide 6 (PA) samples, low molecular weight PA (IPA; $M_n = 15,300$, $M_w = 29,100$) and high molecular weight PA (hPA; $M_n = 22,500$, $M_w = 47,250$), were supplied from Ube Industry and Sumitomo Chemical Industry Co. Ltd, respectively. PE with MAH units (PE-MAH) was supplied from Mitsui Chemical Co. Ltd: Admer NF505; $M_n = 21,400$, $M_w = 69,800$, MAH content = 0.1 wt%, M.F.I. = 0.8 g/10 min. Three random copolymers of ethylene, GMA and vinyl acetate (VAc) were supplied from Sumitomo Chemical Industry Co. Ltd: Bondfast 2A with 3 wt% GMA (E-GMA-3); Bondfast 2B with 12 wt% GMA (E-GMA-12) and Bondfast 2C with 6 wt% GMA (E-GMA-6); VAc content = 5 wt%.

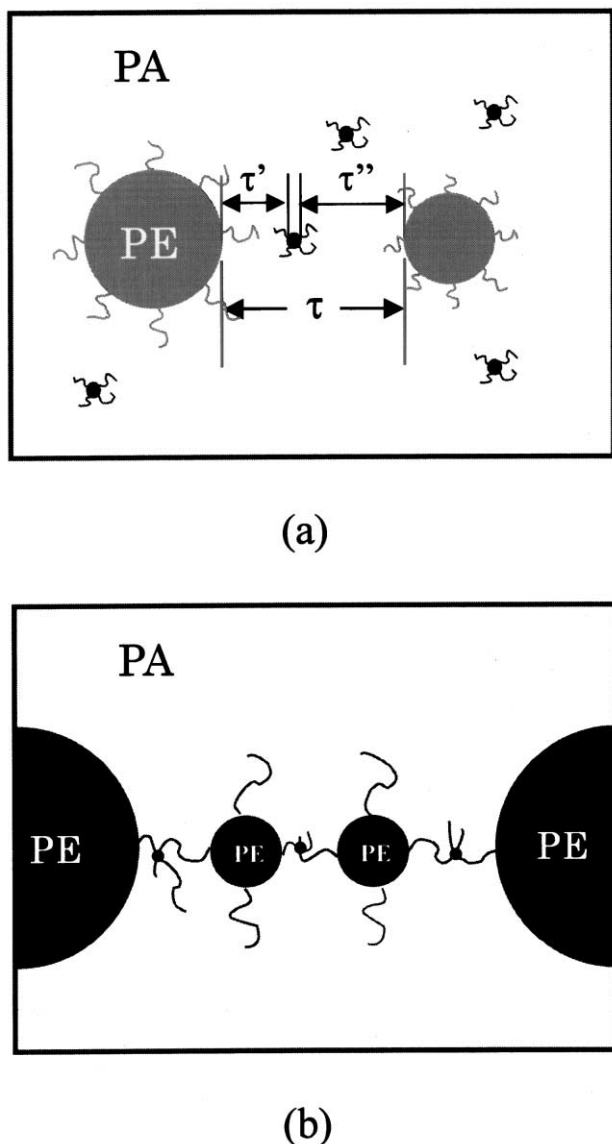


Fig. 2. (a) Reduction of surface-to-surface interparticle distance τ by the presence of micelle ($\tau \rightarrow \tau', \tau''$) and (b) local network formation by a very few tie points in PA matrix via the highly crosslinkable PE domains.

Table 1
Characteristics of component polymers

Component	T_m^a (°C)	η^b (Poise)	M_n (k)	M.F.I. (g/10 min)
hPA	221.9	14,120	22.5	
IPA	222.0	2700	15.3	
PE-MAH ^c	120.0	15,600	21.4	
E-GMA-12 ^d	94.6	11,140		3.0
E-GMA-6	106.5	13,250		3.0
E-GMA-3	96.5	16,710		3.0

^a Melting temperature measured by DSC at heating rate of 10°C/min.

^b Complex melt viscosity at 240°C (7 rad/s).

^c Functionalized PE grafted with MAH; MAH content = 0.1 wt%.

^d Random copolymer of ethylene, VAc, and GMA: number indicates GMA content (wt%), VAc content = 5 wt%.

The complex dynamic viscosity of the component polymers was measured by a Rheometrics dynamic mechanical spectrometer using 25 mm parallel plates under a fixed strain amplitude of 5% at 240°C (Table 1). The gap between the two plates was set at 1.0 mm.

DSC measurement was conducted on a Seiko Exstar 6000 thermal analysis instrument with heating rate of 10°C/min under N₂ flow rate of 5 ml/min.

2.2. Melt mixing

PA pellets were dried under vacuum (10⁻⁴ mmHg) at 80°C for 24 h before mixing. PE samples were also dried at 70°C. Melt mixing was conducted in a miniature mixer of 1 g scale, Mini-Max Molder (CS-183MM, Custom Scientific Instruments Inc.) at 240°C. Rotational speed was set at 50 or 100 rpm, corresponding to a maximum shear rate of 7 and 14 s⁻¹, respectively.

2.3. Electron-beam irradiation and characterization

The as-mixed specimen was melt pressed at 240°C with a spacer to a thin sheet of 30 mm × 5 mm × 1 mm. As soon as it is taken out of the hot stage, the specimen was quenched in ice water. Six sheets for each blend were served for electron beam irradiation.

Electron beam irradiation was carried out on an irradiation apparatus, Sagatron; Nissin Electron Co. Ltd, with the acceleration voltage of 1.2 MV at the rate of 5 kGy/s (1 Mrad = 10 kGy) under doses of 3, 6, 12, 18, 24 and 36 Mrad. Dynamic storage modulus of the irradiated specimens was then measured as a function of temperature, using a dynamic mechanical analyzer, model DVA-200 (IT Meter and Control, Inc.), at a heating rate of 2 K/min and a frequency of 10 Hz. The modulus at 245°C (above T_m of PA) was used as a measure of the degree of crosslinking.

2.4. Morphology analysis

The blend specimen was placed between two cover glasses and melt-pressed at 240°C to obtain a thin film with thickness of ca. 15 μm on a hot stage set on a light scattering apparatus. After melt pressing, the time-resolved measurement of scattering profile (intensity of scattered light vs scattering angle) was made at a time slice of 1/30 s. The scattering measurement was performed by a highly sensitive CCD camera with 576 × 382 pixels, a He–Ne laser of 632.8 nm wavelength and V_v (parallel polarization) optical alignment. A scattering profile just after the re-melt provides information on the morphology. Detail of data analysis is shown elsewhere [9].

For TEM observation, the quenched sample was exposed to ruthenium tetroxide (RuO₄) vapor at room temperature for 2 h and then cryomicrotomed by an ultramicrotome (Reichert Ultracut-Nissei) at –60°C to obtain an ultrathin film of ca. 60 nm thickness. The ultrathin section was then mounted on 200 mesh copper grid and again exposed to the

RuO₄ vapor for another 1 h. Amorphous region of PE was preferentially stained by RuO₄. Morphology was observed by a transmission electron microscope, JEM-100CX (JEOL), under an accelerating voltage of 100 kV. Mean ligament thickness τ was obtained by averaging over more than 200 particle pairs.

3. Results and discussion

Fig. 3 shows TEM micrographs of 70/30 hPA/E-GMA blends after mixing at 240°C for 15 min. The dark region is PE phase stained by RuO₄. There are many tiny domains of ca. 30–50 nm in diameter coexisting with sub- μ m PE particles. The tiny domains may be regarded as micelles of in situ-formed graft copolymers, pulled-out from the surface of PE particles under shear forces during reactive blending. These are the expected results as have been discussed in Fig. 1. The results of morphology analysis are summarized in Table 2, in terms of the average particle size D by light scattering and the surface-to-surface interparticle distance τ by TEM. The higher GMA content in E-GMA yielded smaller D and τ , implying that the more coupling reaction resulted in the more micelles (see Figs. 1d and 2).

The sub- μ m PE particles in Fig. 3 are not circular. The asphericity of PE particles means low interfacial tension caused by good emulsifying effect of in situ-formed graft copolymers remaining at the interface [10].

Fig. 4a shows TEM micrograph of 65/35 hPA/PE-MAH blend (M-4). Tiny PE micelles are seen to coexist with sub- μ m PE particles as in Fig. 3. These are regarded as micelles of inverse Y-shape graft copolymers (Fig. 1b). The values of τ and D listed in Table 2 are slightly larger than those of hPA/E-GMA systems in Fig. 3 (G-series). It may be caused by the lower content of reactive sites in PE-MAH than in E-GMA. Fig. 4b shows the TEM micrograph of 50/15/35 hPA/IPA/PE-MAH blend (M-3) by two-step mixing. In the two-step mixing, IPA was first mixed with PE-MAH at 30/70 for 10 min at a rotor speed of 100 rpm, and then the PE-rich blend was mixed with hPA at 50/50 for 5 min (total mixing time = 15 min.). In the first step, Y-shape graft copolymer should be formed in situ at the interface between dispersed PA phase and PE matrix via coupling reaction (see Fig. 1c). Then, by mixing with hPA at the second step, the PE particles having micelle dispersion should be dispersed in hPA matrix. The micelles occlusion means the ‘fatted’ PE particles for the given PE/PA blend ratio so that the τ could be reduced. However, the result (Table 2) was contrary to our expectation; the τ value (0.8 μ m; M-3) was larger than that by 1-step mixing ($\tau = 0.5 \mu$ m; M-4). This may be caused by non-uniform break-up of the PE-rich mixture in the second step due to its high viscosity arising from micelle formation in the first step, as seen in Fig. 4b. The situation could not be improved by replacing the PA component at the first step by hPA (M-2) and by changing the mixing time program from (10 min/1st and 5 min/2nd)

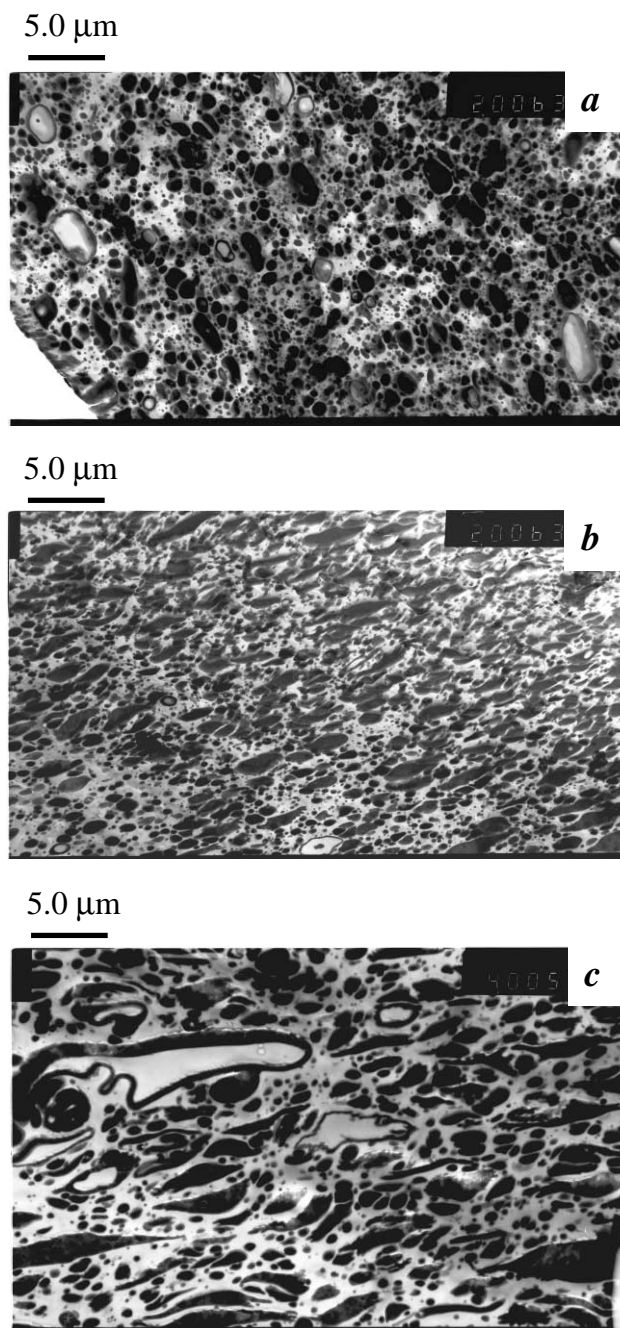


Fig. 3. TEM micrographs of 70/30 hPA/E-GMA blends after 15 min mixing. GMA content in E-GMA: (a) 3 wt%; (b) 6 wt% and (c) 12 wt%; corresponding to the sample codes (a) G-3, (b) G-2 and (c) G-1 in Table 2, respectively.

to (5 min/1st and 10 min/2nd, M-1). Thus, the results were unexpected. However, as a consequence, a series of PE/PA blends having various τ values were prepared. Then, all samples were subjected to electron-beam irradiation to investigate the effect of τ on the electron-beam crosslinkability.

Fig. 5 shows the storage moduli of 70/30 hPA/E-GMA-12 blend (G-1) and component polymers as a function of

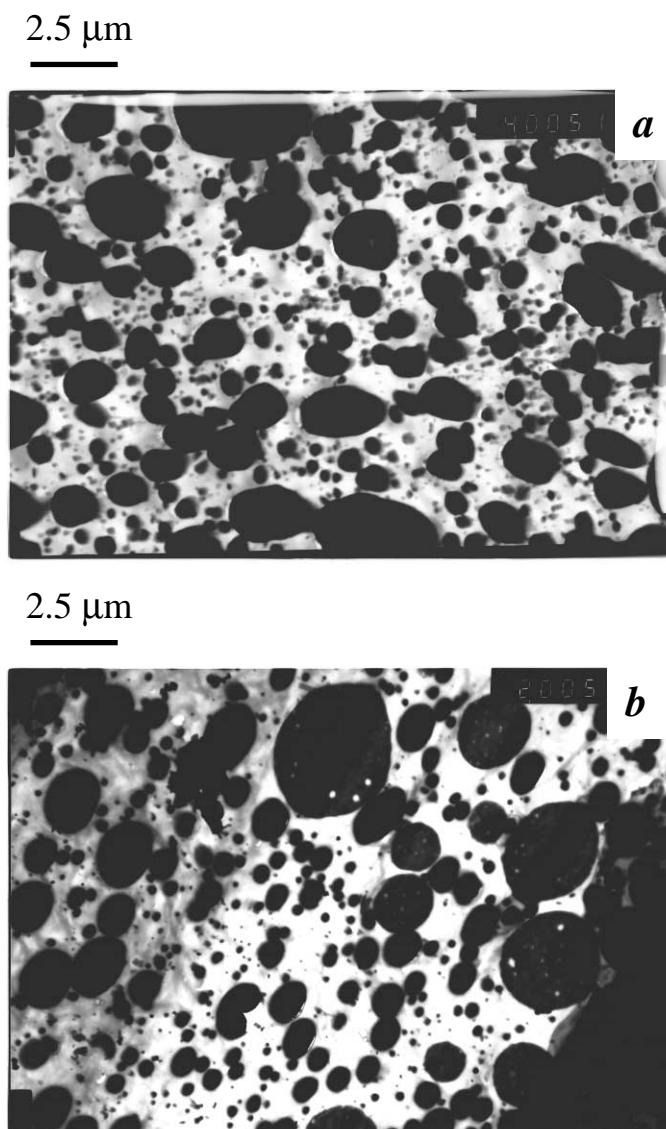


Fig. 4. TEM micrographs of (a) 65/35 hPA/PE-MAH and (b) 50/15/35 hPA/IPA/PE-MAH blends after mixing for 15 min.

temperature. Compared with non-irradiated samples (Fig. 5a), the irradiated samples (Fig. 5b) maintain the rubbery plateau modulus above the melting point of PA ($T_m = 222^\circ\text{C}$), suggesting an establishment of three-dimensional crosslink network by the electron-beam irradiation. Actually, the irradiated specimens were able to shrink back to the original geometry after releasing from the clamps for DMA measurement. The magnitude of the rubbery plateau above T_m should be proportional to the crosslinking density. Then, a modulus at 245°C was employed as a measure of crosslinking density.

Fig. 6 shows the change in the modulus at 245°C (E') with irradiation dose for the M-series samples (Fig. 6a) and the G-series samples (Fig. 6b), together with the component polymers. The E' value increases rapidly in PE but slowly in PA, suggesting that PE is

an easily crosslinkable polymer and PA a hardly crosslinkable one. Blend samples show intermediate behavior. A chain line in Fig. 6 was drawn following a simple additive rule ($w_A \log E'^A + w_B \log E'^B$; w_i being wt fraction). All data points for M-series are located below the additive line (Fig. 6a), while for G-series above the line (Fig. 6b). Note that G-series have less amount of PE component than M-series. Then the results in Fig. 6 suggest that the morphology plays predominant role over the amount of easily crosslinkable component.

In Fig. 7, the rubbery plateau modulus is plotted vs. D for various dose levels. The modulus hardly depends on D at high dose levels. At low dose levels, there is no correlation between the modulus and D .

By contrast, a nice correlation was found between the modulus development and the surface-to-surface

Table 2
Blend composition (wt%), mixing condition and morphology

Sample code	G-1	G-2	G-3	M-1	M-2	M-3	M-4
hPA	70	70	70	65	65	50	65
IPA						15	
E-GMA-12	30						
E-GMA-6		30					
E-GMA-3			30				
PE-MAH				35	35	35	35
Mixing	1-step ^a	1-step ^a	1-step ^a	2-step ^b	2-step ^c	2-step ^c	1-step ^a
D^d (μm)	0.3	0.4	0.7	0.4	0.5	0.7	0.6
τ^e (μm)	0.23	0.30	0.33	0.57	0.65	0.80	0.50

^a 1-step: PE and PA were put into mixer at once and mixed at 240°C for 15 min (rotor speed: 100 rpm).

^b 2-step: hPA (or IPA) and PE-MAH were firstly mixed at 30/70 (PA/PE) wt ratio at rotor speed of 100 rpm for 5 min and then the PE-rich blend was mixed with hPA at 50/50 wt ratio for 10 min.

^c 2-step: the first mixing for 10 min and the second for 5 min.

^d Particle diameter by light scattering.

^e Surface-to-surface interparticle distance by TEM.

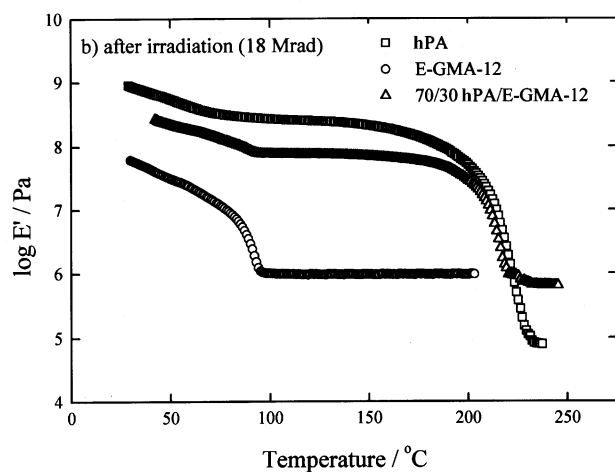
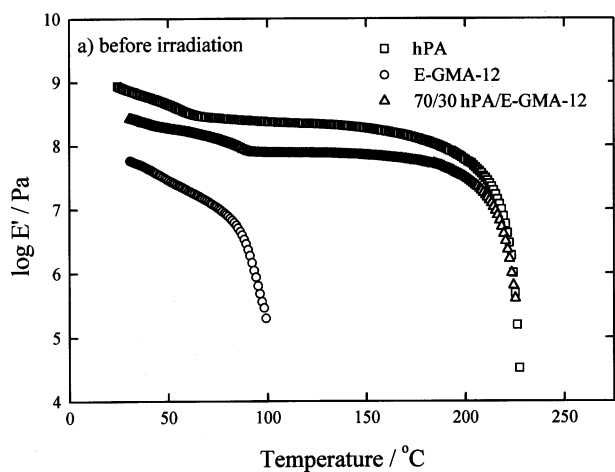


Fig. 5. Dynamic storage modulus vs. temperature: (a) before and (b) after electron beam irradiation at 18 Mrad.

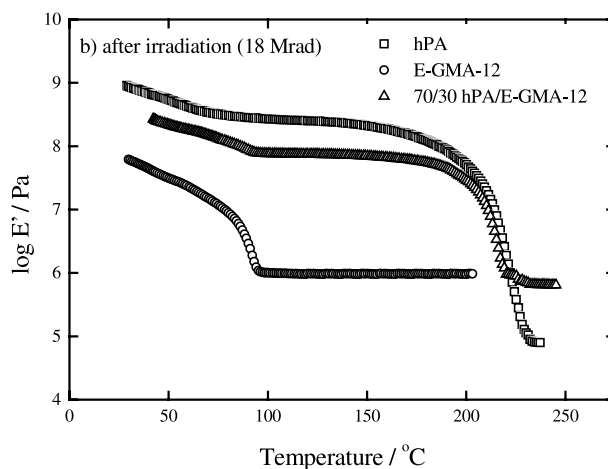
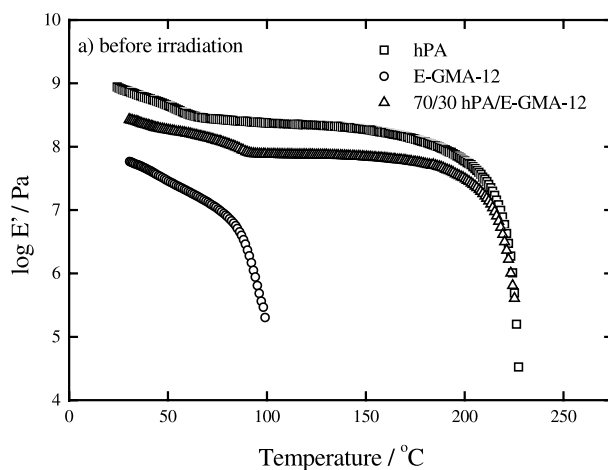


Fig. 6. Change in the dynamic storage modulus at 245°C (above T_m of PA) with electron-beam irradiation: (a) M-series; (b) G-series. Chain line is by a simple additive rule ($w_A \log E'^A + w_B \log E'^B$).

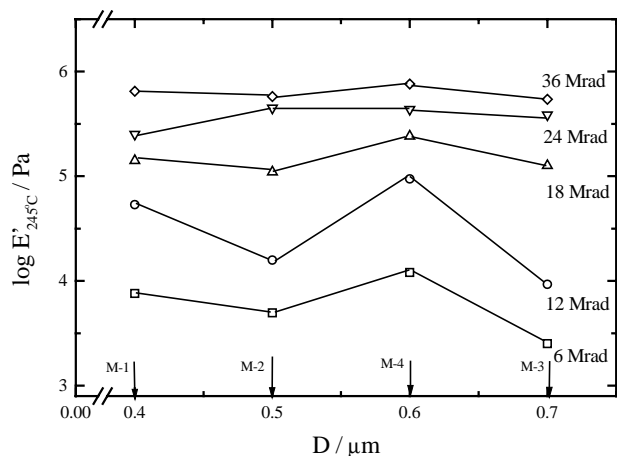


Fig. 7. Dynamic storage modulus at 245°C (∞ crosslink density) vs. average particle size plots.

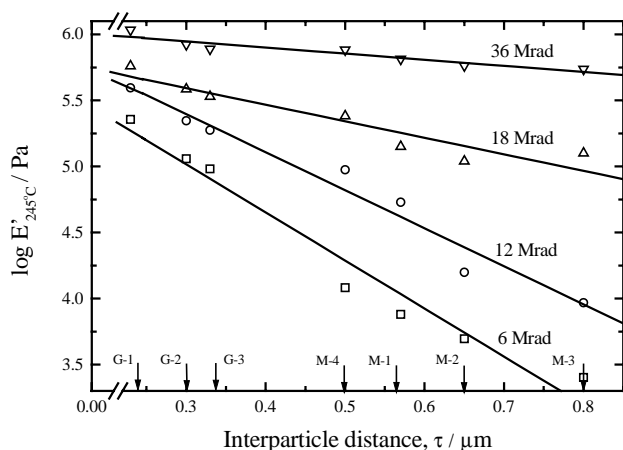


Fig. 8. Dynamic storage modulus at 245°C (∞ crosslink density) vs. surface-to-surface interparticle distance.

interparticle distance τ , as shown in Fig. 8. The shorter τ renders the faster increment of E' at 245°C (the faster crosslinking), as expected from the discussion in Fig. 2.

The situation can be demonstrated more clearly by defining a characteristic dose ϑ_c as schematically shown in an inserted figure of Fig. 9. The ϑ_c may be the dose at which the three dimensional network is established by radiation crosslinking. The shorter the τ , the smaller is the ϑ_c . The blend having the shortest τ has almost same value of ϑ_c as pure PE-MAH and E-GMA. It means the 70/30 PA/PE system can be easily crosslinked as pure PE when the interparticle distance is adjusted to be short enough. It is amazing at the material design point of view.

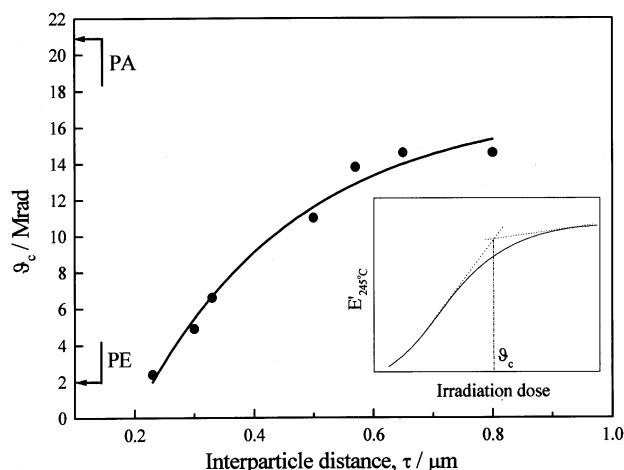


Fig. 9. Plot of the characteristic dose (ϑ_c ; defined as in an inserted figure) vs. surface-to-surface interparticle distance τ .

4. Conclusion

Thus, by blending PA with the ethylene copolymer with many reactive sites, the surface-to-surface interparticle distance τ could be reduced by micelle formation via the pull-out of in situ-formed graft copolymer. The blend with short τ ($\sim 0.2 \mu\text{m}$) was well crosslinked by electron-beam irradiation at low dose level similar to that for PE; even when PA was the major component (70/30) and it was the matrix. The results would be applied for developing high-temperature materials.

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